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Thermodynamic modelling of short and long term hydration of ternary binders. Influence of Portland cement composition and blast furnace slag content

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HIGHLIGHTS

- Thermodynamic modelling confirms the influence of the PC composition.
- Ternary blends with FA are more dependent on the PC composition.
- 40–50% content of BFS in ternary blends is optimal.

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ABSTRACT

Ternary blends are currently used to improve the properties of Portland cement (PC). In this paper, thermodynamic modelling has been used to analyze the influence of the PC composition on the hydrates formed, in binary and ternary blends with blast furnace slag (BFS), and limestone filler (LF) or fly ash (FA) in order to complement experimental results. Thermodynamic modelling shows that contents of 40–50% of BFS can be optimal in ternary blends with low LF or FA content, and modelling also shows the significant effect of the composition of the PC used in the hydration process of the blends.

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1. Introduction

The use of supplementary cementitious materials (SCMs) such as blast furnace slag (BFS), limestone filler (LF) or fly ash (FA) is widespread as it minimizes the energy consumption and the CO₂ emission of the Portland cement (PC) production [1–3]. In addition, after longer hydration times similar mechanical properties as for PC are obtained and durability with respect to sulfate attack and chloride ingress is generally improved [4–6]. The use of two or more SCMs jointly can lead to synergies between them and the PC during the hydration thus promoting optimal properties of the resulting blend [7–10].

Hydration tests at short (<7 days) and medium (<90 days) ages of binders containing SCMs have demonstrated their effect of the composition, particle size and content on the hydration kinetics, the type of hydrates and the mechanical properties generated [7–26]. Besides, it has been demonstrated that the chemical and

mineralogical composition of the PC have significant influence on the evolution of the aqueous pore solution and solid hydration phases formed [9,10]. Better mechanical strength gains at short term (<7 days) in ternary blends has been achieved with a PCs containing low C₃A and/or alkali contents as in [12,13,23] than with PCs with higher contents [8,15,18]. The initial synergy between PC and SCMs in the hydration of ternary blend affects the initiation of hydration reactions, as found in [10] from calorimetry and setting tests.

Models are being developed to complement the hydration experimental studies. The modelling of interactions between solid and aqueous phases on the hydration of cementitious materials using geochemical speciation codes can be the basis for a better understanding of the chemical interactions and of the influence of the SCMs added [7,27]. The reaction of PC with SCMs has been analyzed through thermodynamic modelling and experimentally [7,27–30], studying the changes of pore solution and hydrate assemblage with time [27,29,30] and investigating the effect of type and amount of SCMs after long reaction ages [7,28,29]. The

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thermodynamic models show that BFS causes the destabilization of portlandite at high replacement levels, the formation of C-S-H gel with a lower CaO/SiO₂ ratio and the disappearance of monocarbonate [28], LF causes the stabilization of monocarbonate instead monosulphate, which stabilizes the ettringite with the subsequent improve of the physical-mechanical properties [29] and FA causes the reduction of the total portlandite content [28].

The effect of the mineralogical and chemical composition of the PC on the synergy of hydration in presence of SCMs, at short and long-term ages, is predicted using thermodynamic models. The thermodynamic models are compared with experimental data up to 90 days of hydration [9,10] for verification, in addition to predict the long-term stability. The maximum substitution of BFS varying the PC composition is also studied through thermodynamic models for suitable ternary blends design.

2. Model parameters identification and capture

The geochemical modelling program Gibbs free energy minimisation (GEMS) [31,32] was used with thermodynamic data from the PSI-GEMS database [33,34] supplemented by cement specific data [35–37]. The input parameters for the thermodynamic model are the composition and the reactivity of the PCs and SCMs, the w/b ratio, the curing conditions and the composition of the blends. The amount of Al present in siliceous hydrogarnet (C₃(A,F)S_{0.84}H_{4.32}) was limited to 1 per formula unit following [37]. The pastes considered had a w/b ratio of 0.5, hydrated at 21 °C and 100% RH, similarly to those described in [9,10].

The thermodynamic model needs to implement data of the hydration degree of PCs and the SCMs such as BFS and FA. The reaction of the PC was modelled using the empirical approach of Parrot & Killoh [38] that describes the dissolution of the different clinker phases as a function of time, as detailed in [29,36]. Although this approach does not account for effect of SCM on the reaction kinetic of the PC, it allows following the general hydration kinetics. The parameters of the reactivity of BFS and FA were obtained from a simple pozzolanity tests in a CaCO₃-Ca(OH)₂-KOH system according to [39,40]. CaCO₃ was added to offer a reaction partner for the aluminium in the SCMs and thus to mimic the conditions in the pore solution of a hydrating PC after 1 day or longer. This approach results in a similar reaction kinetics of the SCM as in a PC system as detailed in [39–41]. A mix of 1 g of BFS or FA, with 0.25 g of CaCO₃ and 1 g of portlandite is dissolved in 10 ml of 0.1 M KOH dissolution in order to simulate the pore solution pH value around 13.0 expected in the PCs and blends as measured in [9]. After 1, 2, 7, 28 and 90 days of interaction, the hydration of SCM was stopped by filtration and further drying in isopropanol for 15 min. The excess of isopropanol was removed by filtering with a Buchner funnel and applying diethyl ether. After a short drying for 8 min at 40 °C the samples were stored in a vacuum desiccator under nitrogen atmosphere until analyses. TGA was carried out the same day the samples were stopped with a TGA/SDTA851e from Mettler Toledo. Approximately 50 mg of the samples were placed in open 150 µl alumina ceramic pans and heated from 30 to 980 °C with a heating rate of 20 K/min under nitrogen at a flow rate of 30 ml/min. From the raw data, bound water and portlandite content were calculated with respect to dry sample weight at 550 °C. Details on the calculations are described in [42]. The expected bound water content was calculated by thermodynamic modelling, using the starting materials of the mixes (1 g of SCM, 0.25 g of CaCO₃ and 1 g of portlandite) and different degree of SCM reaction. In this way, the different hydration times could be associated with the percentage of reacted SCM. Table 1 shows the reaction degree (average values) of both SCMs at different ages of hydration. The bound water was chosen as the most reproducible parameter and was calculated from the water loss between 40 and 550 °C

Table 1
Reaction of BFS and FA at 1, 2, 7, 28 and 90 days of hydration.

Time (days)	% Reacted BFS	% Reacted FA
1	3	2
2	8	2
7	20	7
28	29	8
90	66	29

Table 2
Chemical and mineralogical composition (main phases) and CaCO₃ content (wt%) of the raw materials [9,10].

%	OPC-L	OPC-H	BFS	LF	FA
Na ₂ O	0.2	0.1	0.4	0.6	0.8
K ₂ O	0.3	0.9	0.5	2.7	4.5
Na ₂ O _{eq.}	0.4	0.7	0.7	2.3	3.7
CaO	60.3	63.3	45.5	26.1	3.6
SiO ₂	17.4	19.6	36.6	21.4	52.0
Al ₂ O ₃	4.7	5.5	10.4	7.8	24.9
Fe ₂ O ₃	5.1	2.4	0.3	2.6	6.3
MgO	1.8	0.8	7.5	5.8	1.7
SO ₃	3.2	3.2	0.1	0.1	0.2
LoI	4.2	2.5	NA	30.1	NA
C ₃ S	50	53	–	–	–
C ₂ S	12	16	–	–	–
C ₃ A	4	10	–	–	–
C ₄ AF	15	7	–	–	–
CaCO ₃	4	3	<1	61	<1

LoI: Loss on ignition, NA: Not analyzed.

[41,43]. For modelling, the hydration degree at 2 and 90 days of hydration was used, depending on the BFS content, the degree of reaction used for FA and BFS are those given in Table 1. For the modelling of the long-term hydration depending on the BFS content, the degrees of reaction were 100% for PCs (discounting the content in CaCO₃), 75% for BFS and 50% for FA according to [28]. This corresponds to the reaction degree generally observed after 1 year or longer, although the actual reaction degree might be slightly different [44]. In all case modelled, the limestone is considered to react without restrictions, and in order to simplify the calculations and due to the main objective of this paper in the study of the influence of the PC composition and of the BFS content, no distinction between reactive and non-reactive phases of FA has been made.

The thermodynamic model results have been compared with some experimental results: X-ray Diffraction (XRD) and differential thermal and thermogravimetric (DTA/TG) analysis in pastes and mechanical strengths in mortars [9,10]. The thermodynamic modelling was carried out for the two PC CEM I with different chemical and mineralogical composition. The SCMs considered were BFS, FA and LF. The chemical composition and mineralogical composition of both PCs and SCMs used for the thermodynamic hydration models were described elsewhere [9,10] and reproduced in Table 2 for the convenience of the reader. The mineralogical composition was estimated through Bogue equations [45], after correction taking into account the CaCO₃ content (4% for PC-L and 3% for PC-H). The CaCO₃ and gypsum contents (3% for PC-L and 2% for PC-H) were calculated by thermogravimetric analysis.

The PC with low alkali (0.4% of Na₂O_{eq.}) and C₃A content (4%) was labeled “L”, while the PC with higher contents (0.7% of Na₂O_{eq.} and 10% of C₃A) was labeled “H”. In addition, the C₄AF content (15% in PC-L and 7% in PC-H) is significantly different between the two PCs. The three SCMs had higher alkali and Al₂O₃, and lower SO₃ contents than the PCs. LF had a CaCO₃ content of 61% and FA had low calcium content. The two PCs were chosen to have a similar particle size distribution measured by laser diffraction spectrometry as described in more detail in [9,10] in order to avoid

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